PHENOLS AS CHEMICAL FOSSILS IN COALS

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Introduction

It is generally considered that vitrinite, the principal maceral in most coals, represents coalified, partly decayed wood. Hence lignin should be one of the important precursors to the vitrinites in coals. Accordingly, it would be interesting to know whether any chemical fossils related to lignin could be found in coals. The purpose of this paper is to report what we believe to be a successful search for such fossils. The experimental approach exploited a degradation reaction developed in a study of soil humic acids by Burges et al.[1]

This reaction involves a reduction degradation with sodium amalgam and hot water. Thin layer chromatography of the ether soluble part of the product (yield, about 20%) showed the presence of a number of phenols and phenolic acids, most of whose structures bore obvious relationships to known microbial and chemical degradation products of lignin (I) but some to the A ring of flavonoids (II).
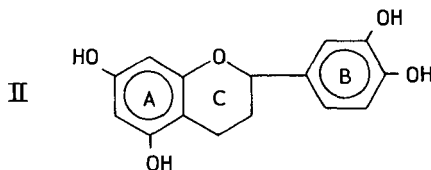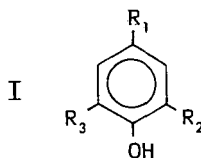
where R_1 = COOH, CHO, -CH=CH-COOH, -CH-CO-COOH, etc.; R_2 = H or OCH_3 or OH; R_3 = H or OCH_3 or OH. The R_1 group may represent a side chain of 1, 2 (rarely) or 3 carbon atoms, in various states of oxidation. Burges et al. therefore concluded that the humic acids they studied were condensates of phenolic compounds from the degradation of plant products with amino acids (see also Flaig[2]).

Humic acids can be extracted from peats and lignites but not from bituminous coals. However, oxidation of bituminous coals with aqueous performic acid generates in high yield (80-110% by weight) materials that closely resemble humic acids[3]. In preliminary studies performed some years ago by one of us (J.B.) while on leave of absence from his Institute, the Burges reductive degradation was applied to humic acids extracted from some peats and lignites, and produced by oxidation of a number of bituminous coals. A number of identifications of products were made by gas chromatography with co-injection of standards, but at that time facilities were only rarely available to permit confirmation by mass spectrometry. Such confirmation has been more fully obtained recently by another of the authors (S.R.), who also studied a wider range of coals (totalling 43 samples).

It is proposed in this preliminary publication to describe the experimental procedures and to give a sufficient selection of the data to show what was found by co-injection and later confirmed by mass spectrometry.

The major coal measures of the United States were laid down either in the Carboniferous era (ca. 300 m. years B.P.), or in the Cretaceous and Tertiary (130-60 m. years B.P.). Between these two eras a great deal of evolution occurred in the plant kingdom; associated with this were some changes in the nature of groups R_2 and R_3 in structure I above. However, having stated the fact, we need not pursue this matter here.

Experimental

Humic acids were extracted from peats and lignites with 0.5N sodium hydroxide following standard procedures.

The oxidation of coals with aqueous performic acid is highly exothermic. Five gm of coal was dispersed in 50 ml of anhydrous formic acid, and 50 ml of 30% hydrogen peroxide was added in 2 ml portions at such a rate that the temperature did not exceed 55°C (however, in the earlier phase, the coal/ formic acid suspension was cooled in ice during the addition of H_2O_2). The mixture was then allowed to stand at room temperature with stirring for 24 hours. The washed and dried solid product was extracted with 1N NaOH under nitrogen and centrifuged. The extract was precipitated by acidification to pH 1. The washed and dried humic acids were redissolved in alkali and, following the procedure of Burges et al.[1], treated with 3% sodium amalgam while the solution was heated in an oil bath at 110-115° for 4-5 hours.

After removal of mercury, the resulting solution was acidified to pH 1 and centrifuged; the supernatant was carefully removed and the residue extracted twice by centrifugation with ether and twice with methylene chloride. Solvents were removed and the residues mixed. The residues were treated with Sylol HTP reagent (Supelco, Inc., Bellefonte, Pa.) under the conditions recommended for converting phenols to trimethylsilyl ethers and carboxylic acids to the corresponding esters.

Experiment showed OV 101 column packing (3% on 80/100 mesh Supelcoport) to be the most effective for gas chromatography of the six packings tested. GC analyses, with and without co-injection of standards, were performed with a Hewlett-Packard No. 5750 instrument, equipped with flame ionization detectors. GC/MS analyses in the later phase were made by Mr. David M. Hindenlang, using a Finnegan model 3000 instrument under the charge of Dr. Larry Hendry of the Chemistry Department of this University. OV 101 columns were again used. The GC/MS instrument was provided with a data system, and this was used to subtract the mass spectrum at the foot of each peak just before it began to elute, or just after it had done so, from the spectrum recorded as the maximum of the peak was eluted. Such a procedure is certainly arbitrary, but disc space could not be monopolized for continued storage of our data while other procedures were tested and interpretations worked out. Consequently, the raw MS data, massaged as described above, were reported for standards and unknowns as printouts tabulating m/e values and relative intensities, and comparisons were made by visual inspection of the printed data.

Results

On the dry basis the weight of crude oxidized coal was usually 85-105% of the weight of raw coal. The yields of daf humic acids were in the range 65-90% of dmmf coal. Within the range of rank studied (78-87% C dmmf), the yield tended to increase with increasing rank. Petrographic studies of the

oxidized products of three coals (by Dr. Alan Davis and Mr. Harrey Zeiss, to whom we are indebted) showed that the vitrinites were greatly altered compared with their appearance in the raw coals, while sporinite and the inert macerals had changed little or not at all. These apparently unaltered macerals could still be recognized in the NaOH-insoluble materials. Thus the humic acids were derived very largely from the vitrinitic macerals. The yields of ether soluble products from the reductive degradation were in the range 10-40% of the weight of humic acids taken; yields when the reaction is applied to soil humic acids were about 20%.[1] Yields from humic acids from the younger Western coals tended to be somewhat higher than those from Carboniferous coals of the eastern U.S.

Chromatograms obtained in the earlier phase of the work are shown in Figures 1 and 2, where the names of compounds identified, mostly by co-injection, are entered against the corresponding peaks (trivial names are used in the figures because they are usually shorter; a list of equivalent systematic names is given in the Appendix, Comparison of the structures with I and II above will show which may be biologically related). It will be seen that resolution is moderately good but that even so a number of major peaks are unidentified.

These curves are typical of what was found for products from the six coals studied. All 3 dihydroxy-benzenes were commonly found and 2 of the trihydroxy-benzenes. 2,6-Xylenol was frequently found in both the earlier and later work, and was the only one of the six xylenols to be identified. Several of the compounds frequently encountered (vanillin and vanillic acid, syringic aldehyde and acid, p. hydroxy-benzoic acid) are well known as degradation products of lignin. A peak is seen in Figure 1 labelled 2,5-dihydroxy-benzoic acid (2,5-DHBA), and another labelled 2,4-, 3,4-, 3,5-dihydroxy-benzoic acid. Experiments with known compounds showed that the latter three isomers could not be resolved under the conditions used. Later work, using GC/MS, showed that of the three only the 3,4-isomer was in fact present, and this is lignin-related. However, the 2,5-isomer is not, though it could be derived from the A ring of flavonoids, 2,3,4-Trihydroxy-benzoic acid has no obvious biological associations, though the 3,4,5-isomer (gallic acid) occurs widely in the plant kingdom (both isomers were identified).

When, later, a wider range of samples was studied (with somewhat more severe conditions of oxidation), some very poorly resolved chromatograms were obtained; the products evidently often represent very complex mixtures of substances. Surprisingly, the products from nearly all of the younger western coals were resolved poorly or very poorly, while the resolution of those from the Interior and Eastern provinces ranged from mediocre to good. Representative examples of each type are shown in Figures 3 and 4. The resolution in Figure 3 is so bad that one might question whether any identifications are possible. In Table 1, we have assembled details of the mass spectra of four substances alleged to be identified from the GC/MS run shown in Figure 3, with details of the spectra of the standards. The agreement is surprisingly good, and the identifications are, taken with matching of retention times, reasonably secure. When resolution is better, as in Figure 4, one can surely be confident in the identifications; examples of the correspondence of mass spectral data are shown in Table 2.

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It should be added that even when the GC/MS system is used, many prominent peaks remain unidentified. However, many of these showed fragments of m/e=73 in the corresponding mass spectra, so that they evidently contained the trimethylsilyl group and were therefore phenols or acids or both.

In considering the origin of the substances shown as identified in Figures 1-4, one must assume with bituminous coals that carboxylic acid groups result entirely from the performic acid oxidation. There is every reason to suppose that some of the hydroxyl groups were present as such in the raw coals, but one must necessarily enquire to what extent is new OH introduced by the oxidation (performic acid is a known reagent for converting alkenes to epoxides and cleaving them; this process occurs by a concerted electrophilic mechanism. However, the mechanism of attack on coals could be quite different and might, for example, follow a free radical mechanism).

The substances named in Figures 1-4 can be arbitrarily classified as follows: (1) "non-committal" substances - those like phenol, p. cresol and benzoic acid, whose structures are relatively simple and contain no obvious clues to origin, (2) those whose structures could obviously be related to biological precursors, such as vanillic, syringic, ferulic and other substituted cinnamic acids, (3) those whose structures are relatively complex but do not display any obvious association with biological precursors, such as the dimethyldihydroxybenzene shown in Figure 1 (isomers not identified). Of these classes, (1) requires no further comment here, while (3) presumably may include - or consist largely of - compounds whose OH groups are an artefact of the oxidation process. This leaves open the question, to what extent are the compounds of class (2) chemical fossils or artefacts?

Many of the substances identified have methoxyl groups in the 3-position or the 3,5-positions, as in lignins. These groups could hardly have been introduced by the performic acid oxidation, and therefore indicate a chemical fossil status for the substances. On the other hand, Blom et al.[4] state that methoxyl groups are eliminated by metamorphism in the subbituminous range. We must admit that the structures we identify as methyl phenyl ethers represent a small weight fraction of the whole coals: but can also point out that Blom et al. present no evidence that the Zeisel procedure, which they used in their analyses, was completely effective (the reagent HI may not have penetrated the pore structure fully), or even that it produced with coals the results found with simple compounds. Whatever the mechanism of the performic acid oxidation with coals, one would expect that if it introduces new OH groups, more than one isomer would usually be produced. Therefore, where a peak in the chromatograms was identified as due to a lignin-related substance like vanillin or caffeic acid, the mass spectra corresponding to neighboring chromatographic peaks were carefully examined to determine whether they could represent spectra of position isomers. Such isomers were rarely detected. On the other hand, some of the relatively complex substances not obviously related to biological precursors evidently did have isomers present.

We conclude that some of the OH groups in the products may well have been introduced by the performic acid oxidation, but that most of the substances of structure related to lignins were probably not artefacts.

The question, to what extent do the findings reported here relate to the composition of whole coals, must be left for discussion in a later paper when a more complete set of data can be presented. In concluding this paper, we

should draw attention to some implications of the findings, if the provisional assumption can be made that the findings do indeed have relevance to the structure of vitrinite macerals in coals:

1. o-Dihydroxybenzenes, and still more trihydroxybenzenes, are notoriously easily oxidized. This, if such structures are indeed present in vitrinites, we could explain why it is so difficult to nitrate or sulfonate coals, even with mild reagents, without accompanying oxidation[3], and also why coals so readily oxidize in weathering. Partially methylated polyphenols are less reactive, but still quite readily susceptible to oxidation.

2. *Ortho* - dihydroxybenzene derivatives are capable of chelating boron and other elements. Less information is available about o.hydroxy-methoxy derivatives, but there seems no reason why they should not be capable of chelation.

3. During catalytic hydrogenation of coals of any rank to liquid fuels, under conditions that give high conversion, a substantial fraction of the oxygen is removed. However, in interactions of coal with hydrogen donor solvent alone, or in applications of the SRC process, oxygen removal is less complete and the products may retain o.dihydroxybenzene structures, a point perhaps worthy of note by those concerned with the composition of coal liquids.

It is worth noting here that in a study of the products of laser pyrolysis of coals in the ionization chamber of a time-of-flight mass spectrometer, homologous series of what appeared to be dihydroxybenzenes were noted[5]. The technique could not distinguish positional isomers, but the finding is suggestive when taken with the data in this paper.

Acknowledgements

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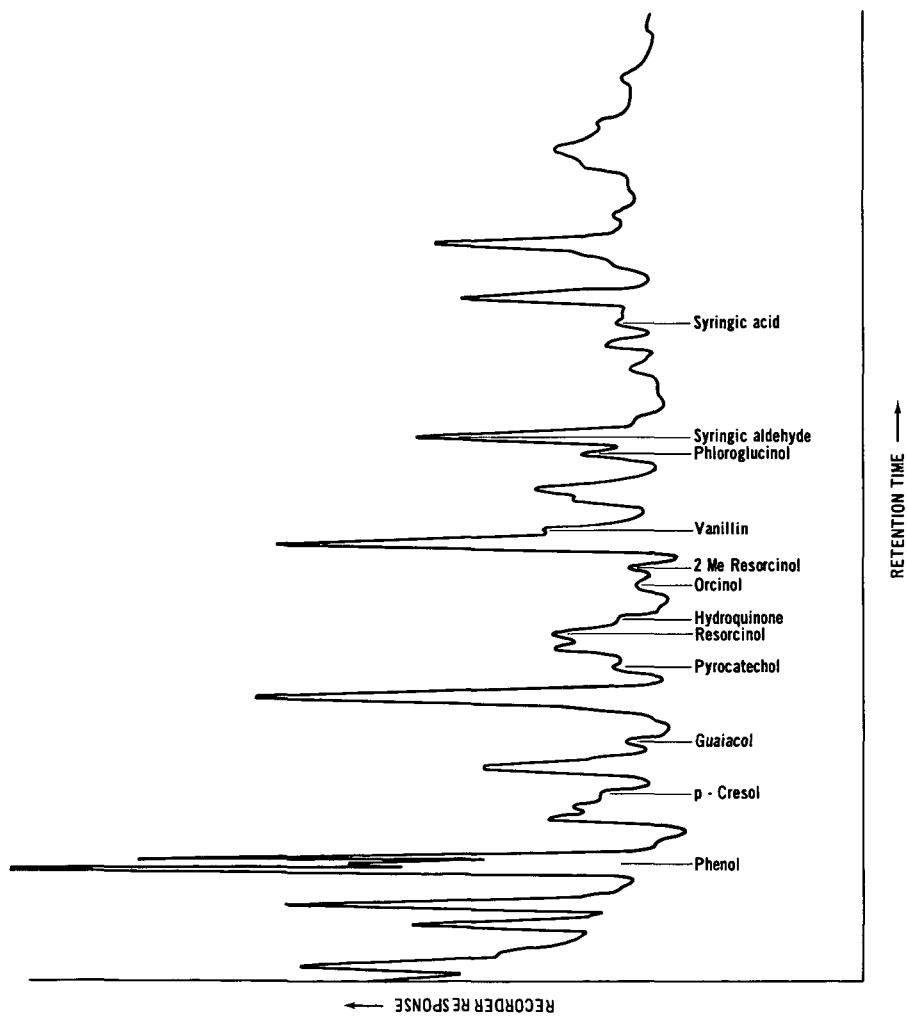
Figure 1. CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM C SEAM COAL, BENHAM, KENTUCKY (HVA, PSOC 13)
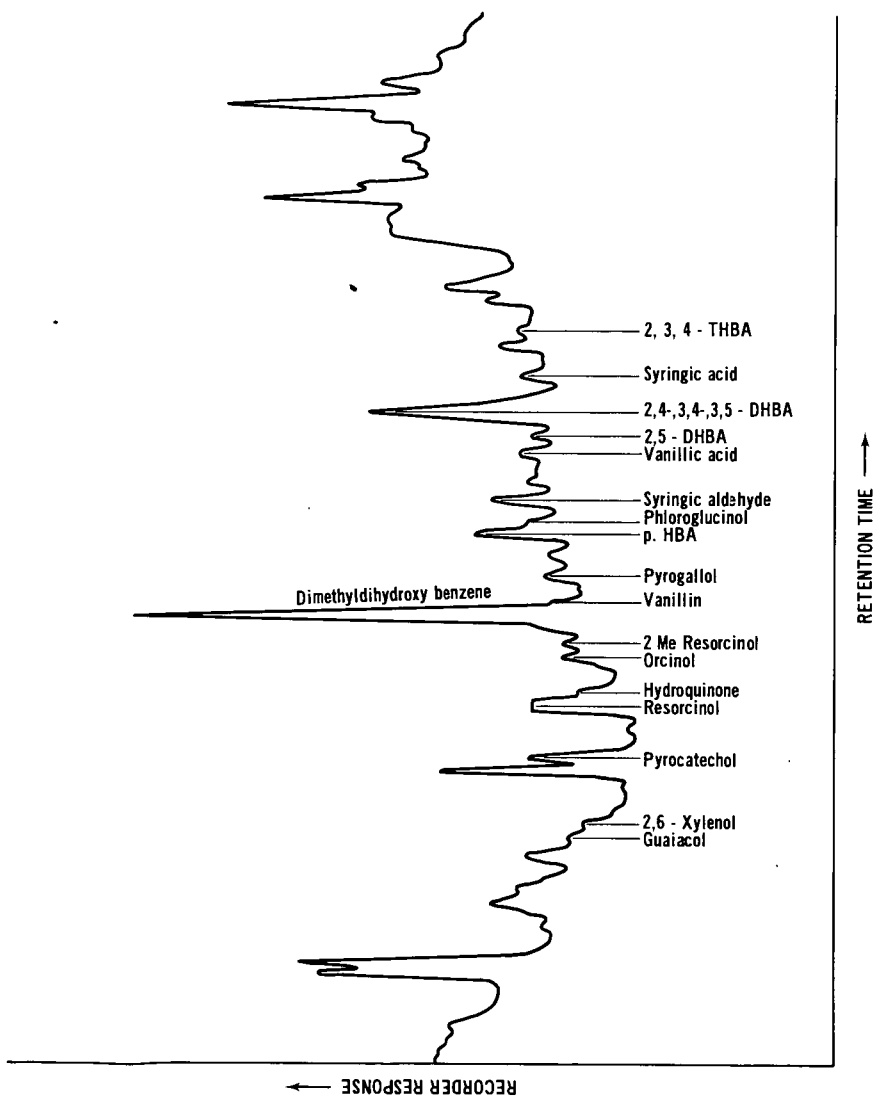
Figure 2. CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM WYODAK SEAM COAL, GILLETTE, WYOMING (sbb., PSOC 100)

The chart has the following labels from top to bottom:

2, 3, 4 - THBA
Syringic acid
2,4-,3,4-,3,5 - DHBA
2,5 - DHBA
Vanillic acid
Syringic aldehyde
Phloroglucinol
p. HBA
Pyrogallol
Dimethyldihydroxy benzene
Vanillin
2 Me Resorcinol
Orcinol
Hydroquinone
Resorcinol
Pyrocatechol
2,6 - Xylenol
Guaiacol

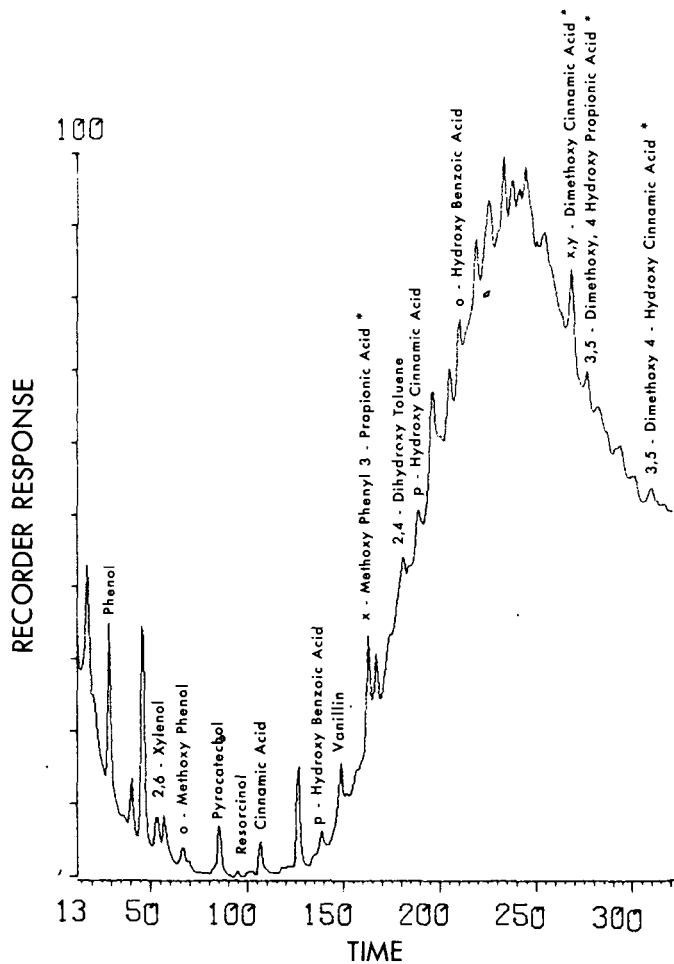RETENTION TIME ⟶

RECORDER RESPONSE ⟵

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Figure 3. TOTAL ION CURRENT CHROMATOGRAM OF DEGRADATION PRODUCTS (AS TMS DERIVATIVES) FROM RED SEAM (HVC), KAYENTA, ARIZONA (PSOC 312)
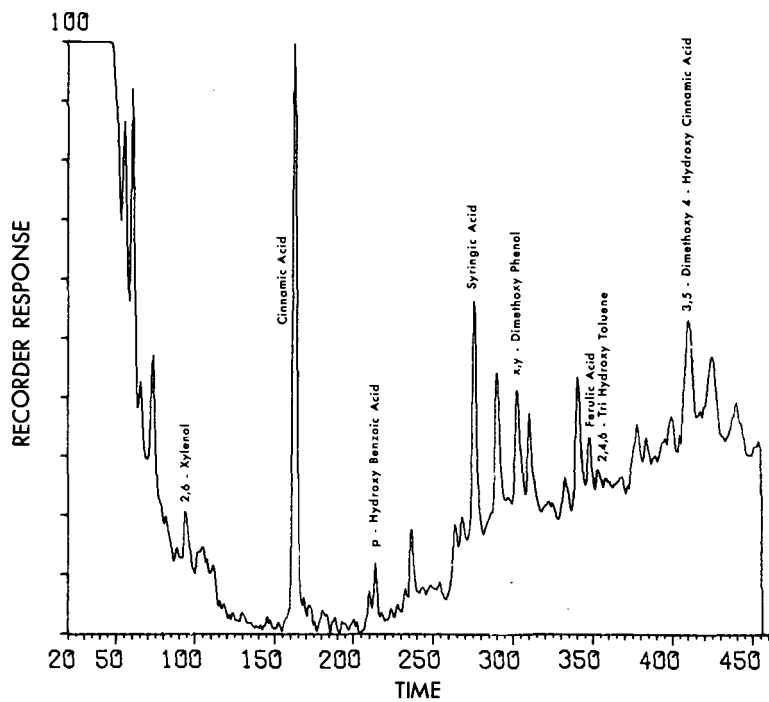
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Figure 4. TOTAL ION CURRENT CHROMATOGRAM OF DEGRADATION PRODUCTS
(AS TMS DERIVATIVES) FROM OHIO NO. 1 SEAM (HVC), JACKSON,
OHIO (PSOC 202)

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Table 1

Data for MS Identification of Substances in Degradation Products of Coal from Black Mesa, Arizona (HVC)(PSOC 312)

	Cinnamic Acid			p. Hydroxybenzoic acid	
m/e	Standard	Unknown	m/e	Standard	Unknown
p/p+1	3.98	4.13	p/p+1	3.28	2.73
205	100	100	73	100	100
57	82	86	193	45	63
45	48	39	267	44	59
145	27	23	223	42	56
55	25	20	45	21	41
89	20	16	75	15	23
67	18	14	126	13	17

	Vanillin			p. Hydroxycinnamic acid	
m/e	Standard	Unknown	m/e	Standard	Unknown
p/p+1	6.95	5.15	p/p+1	6.00	5.27
194	100	88	13	100	83
23	83	100	219	76	100
193	53	45	235	61	79
209	37	60	293	32	41
151	29	38	191	21	39
45	27	33	45	16	25
165	9	17	75	15	19

Table 2

Data for MS Identification of Substances in Degradation Products of Coal from Ohio No. 1 Seam (HVC)(PSOC 202)

	p. Hydroxybenzoic acid			Syringic acid	
m/e	Standard	Unknown	m/e	Standard	Unknown
p/p+1	3.28	3.18	p/p+1	3.72	3.15
73	100	100	73	100	100
193	45	52	45	18	29
267	44	48	141	15	23
223	42	41	327	12	19
45	21	34	312	10	13
75	15	19	89	10	15
126	13	14	297	9	10

	Ferulic acid	
m/e	Standard	Unknown
p/p+1	2.71	2.93
73	100	100
75	48	49
117	38	35
225	24	32
181	22	30
129	22	25
297	20	31

Appendix. <u>Trivial and Systematic Names of Relevant Phenolic Substances</u>

resorcinol	1,3-dihydroxybenzene
pyrocatechol	1,2-dihydroxybenzene
phloroglucinol	1,3,5-trihydroxybenzene
pyrogallol	1,2,3-trihydroxybenzene
orcinol	3,5-dihydroxytoluene
2-methyl resorcinol	2,6-dihydroxytoluene
guaiacol	2-methoxyphenol
vanillin	3-methoxy-4-hydroxybenzaldehyde
vanillic acid	3-methoxy-4-hydroxybenzoic acid
syringic acid	3,5-dimethoxy-4-hydroxybenzoic acid
cinnamic acid	phenyl-3-propenoic acid
ferulic acid	3-methoxy-4-hydroxyphenyl-3-propenoic acid
caffeic acid	3,4-dihydroxyphenyl-3-propenoic acid